Transition Metal Defect Behavior and Si Density of States in the Processing Temperature Regime

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Abstract

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    In order to make predictive models of transition metal gettering during semiconductor processing, a complete understanding of the process variables in high temperature ranges is essential. These variables are the internal gettering site density and capture radius, the intrinsic metal solubility, silicon doping level, the band gap, the effective density of states of the conduction and valence bands, and the transition metal defect level position in the gap. The least understood of these parameters is the temperature dependence of the transition metal defect level position. The work of Gilles et al and McHugo et al demonstrates that the doping enhancement of the solubility of Fe in p-type silicon vanishes at temperatures above 1000ºC. They model this behavior by proposing movement at high temperature of the defect level for interstitial Fe from within the energy gap into the valence band. We explore the available models for Si effective density of states as a function of temperature and generate a third density of states model based on 0 K *ab initio* band structure calculations with the temperature appropriate carrier occupations given by Fermi-Dirac statistics. We also consider uncertainty in E_G in the processing temperature regime. We show that uncertainties in the Si intrinsic properties database in the processing temperature regime can account for the available dopant enhanced solubility data by assuming that E_T remain at a constant fraction of E_G. To quantitatively model gettering processes at high temperatures, more reliable estimates are needed for the densities of states of the conduction and valence bands, E_G and the behavior of defect levels as temperature rises.

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I. INTRODUCTION

The presence of transition metals in silicon device processing has deleterious effects on performance, yield and reliability. In silicon photovoltaics, we are concerned with the impact transition metals have on minority carrier lifetime and thereby efficiency. For integrated circuit applications, we are concerned with gate oxide integrity and device parameter homogeneity across a wafer. For this reason, a quantitative understanding of transition metal equilibria and kinetics at high temperature is needed in order to design gettering processes through accurate simulation. We explore the case of interstitial Fe (Fe_i), however, the method is quite general and can be extended to other deep level impurities in a semiconducting host.

Researchers measuring Fe dopant induced solubility enhancement in p-type Si have found the enhancement to be less than they expected at temperatures ~1000 C and have proposed an instability of the well known Fe_i defect level (E_T) as these high temperatures are approached.[1,2] However, in order to infer the behavior of Fe in the processing temperature regime, we first need to complete our understanding of silicon at these temperatures.

In order to model dopant enhanced solubility of defects in Si quantitatively, we need to understand the temperature dependence of the various defect levels and Si parameters with precision. With regard to the defect Fe, E_T, the Fermi level (E_F), and the intrinsic carrier concentration (n_i) are the controlling parameters. The Si materials parameters, E_F and n_i, in turn depend on the effective density of states (DOS) of the conduction and valence bands (N_C and N_V, respectively) and the semiconductor band gap (E_G). In the work presented here, we demonstrate that uncertainties in the Si intrinsic properties database in the processing temperature regime can account for the available dopant enhanced solubility data by assuming that E_T remain at a constant fraction of E_G.

II. DOPING ENHANCED SOLUBILITY

Heavy p-doping increases the solubility of donor, interstitial transition metal impurities. This effect is driven by electron-hole equilibria and defect pairing to ionized acceptors which we model with defect reactions.[3-7] The intrinsic solubility of Fe in Si [8] represents the undoped reference level. The solubility in silicon is governed by the equilibrium between Fe from an external source with Fe_i donors in solid solution in the Si matrix. In p-type silicon, increased ionization of Fe_i and pairing of Fe_i^+ to ionized acceptors (A_s^-) contributes to solubility enhancement.

The quantitative calculation for the ratio of ionized to neutral charge states for Fe_i is given by Fermi-Dirac statistics for the defect level. The equilibrium constant for ionized $Fe_i^+ \times A_s^-$ pair formation is given by Kimerling et al.[9] Increased p-type doping increases dopant enhanced solubility by moving E_F with respect to the Fe_i ionization level. As more Fe_i is positively ionized, pairing becomes more likely.

III. Si IN THE PROCESSING TEMPERATURE REGIME

Our interest in Si can be categorized into three temperature regimes: *measurement, device operation,* and *processing*. Most of our theoretical and experimental understanding of silicon is from very low temperatures, approximately 0 K – 400 K, in the *measurement* temperature regime. This temperature regime overlaps reasonably with the temperature regime of *device operation*, predominantly between 200K and 500K, providing accurate data for device simulation. For the case of the much higher temperatures of the *processing* temperature regime, approximately 700 K – 1300 K, simulations currently rely heavily on extrapolations from the measurement temperature regime. In order to predict the interaction of defect levels with E_F, we need to understand the variation of N_C, N_V, and E_G at high temperature. It is necessary to extrapolate currently available values of these parameters well beyond the range of available measurements. In doing so, we gain an appreciation for the how the uncertainty at processing temperatures will affect our calculations for dopant enhanced solubility of Fe in Si.

The available models for N_C and N_V show disagreement even in the measurement temperature regime. The routinely used $T^{3/2}$ model found in classics such as Sze's Physics of Semiconductor Devices [10] is based on a parabolic band approximation. Si, however, is known to deviate from this approximation even at low temperatures. The valence band most strongly defies this categorization due to a lack of parabolicity in energy, anisotropy in the constant energy contours and the effect of spin-orbit coupling. At processing temperatures, the parabolic approximation is inadequate for both N_C and N_V. A more realistic empirical fit to data up to 500K is provided by Green.[11] While the Green relation is a better fit to experiment, it is only valid to 500 K and it is not valid when the Boltzmann approximation breaks down, such as in the case of degenerately doped material. This limitation is due to the fact that density of states effective mass is, in general, both temperature and energy dependent (see, for example [12]).

In order to generate a more physically reasonable method for E_F determination in the processing temperature regime, we determine the 0 K DOS from first principles using density functional theory within

the local density approximation (LDA) with the Vienna *ab inito* simulation package (VASP). [13,14]

VASP numerically solves the LDA Kohn-Sham equations using ultra-soft pseudopotentials [15,16] and a

plane wave basis set. A cut off energy of 300eV was used. The exchange and correlation functional was

that of Ceperley and Alder [17] as parameterized by Perdew and Zunger. [18] k-space sampling was

performed with the method of Monkhorst and Pack [19] using an 18x18x18 grid. k-space integrations were

performed using the linear tetrahedron method including corrections according to Blöchl et al.[20] We

perform a rigid energy shift to correct for E_G which is well known to be underestimated by LDA. We then

use Fermi-Dirac statistics (F-D) with numerical integration and $E_G(T)$ to determine $E_F(T)$ as dictated by the

charge neutrality condition. Certain limitations of the calculation include neglecting spin-orbit coupling

and greater inaccuracy in calculating excited states. On the other hand, this method can be used in the

degenerately doped regime without resorting to the parabolic band approximation. In Figure 1, we

compare the calculated DOS with those given by a parabolic approximation to illustrate that they are very

different even in the regions near the valence and conduction band edges.

There are additional concerns with DOS modeling at processing temperatures. All three of these models

rely on the assumption that the band structure is not significantly altered as temperature increases. In the

processing temperature regime, we need to consider the influence of phonons on the band structure. Other

factors that also need consideration are thermal expansion and the influence of the energy level occupations

found at high temperature. The method we have developed for modeling DOS as a function of temperature

is a physically reasonable starting place for determining E_F in the processing temperature regime, but it is

by no means an ending point.

In Figure 2, we compare E_F for both the case of intrinsic Si and for Si with an acceptor concentration

(N_A) of 10^{19} cm^{-3} using the three DOS models discussed. The estimate using the *ab initio* calculated DOS

falls between the curves calculated with N_C and N_V by the $T^{3/2}$ model and the extrapolation of Green's

relations. It is important to note that E_F is quite sensitive to the DOS model used, varying by more than 0.1

eV at the highest temperatures shown.

Since E_F is not a measurable quantity, we look at estimates of dopant enhanced solubility generated

using the different DOS models. Figure 3 displays calculations of Fe solubility for $N_A = 1.5 \times 10^{19}$ cm^{-3} with

each DOS model assuming E_T remains at a constant fraction of the gap. The solid line shows the intrinsic

Fe solubility. The curve predicting the greatest dopant enhanced solubility was generated using again the $T^{3/2}$ model, however for this case, the Boltzmann approximation is used to determine E_F. The significant difference between this curve and that of the same DOS model with F-D integrals determining E_F demonstrates the importance of using the appropriate carrier statistics. Due to the extremely high doping level, F-D are needed.

Also in Figure 3, we overlay the data of McHugo et al. The data is fit within error by the calculations using our DOS method and the $T^{3/2}$ model, with no instability of E_T required. The calculation using the Green extrapolation underestimates for the data point at 1000 C. The $T^{3/2}$ model when used with the Boltzmann approximation overestimates the concentration at 1100 C.

The last parameter we require knowledge of in the processing temperature regime is E_G. Again, we have no reliable expression at these extreme temperatures. That most commonly used was derived by Varshni [21] with fitting parameters valid to 750 K extracted by Alex et al.[22] We have used this relation in the calculations above, but note that extrapolations of empirically based polynomials beyond their regime of validity are notoriously unreliable.

A semi-empirical expression has been developed [23, 24] and fit [25] over the 0 K - 300 K temperature range. Extrapolations to higher temperatures are consistent with extrapolations of a linear fit valid up to 415 K.[10] The extrapolations of these relations from 415 K- 750 K diverges significantly from the expression based on Varshni's model. Nevertheless, we calculate dopant enhanced solubility comparing the two sets of $E_G(T)$ to observe the impact that uncertainty in E_G has on our predictions. Figure 4 shows these results where again we assume E_T remains at a constant fraction of the gap and we use the $T^{3/2}$ model for N_C and N_V. Note that for the data point at 1100 C, the semi-empirical E_G calculation is no longer within error.

IV. DEFECT PROPERTIES IN THE PROCESSING REGIME

In addition to the temperature dependence of fundamental properties of the host material, quantitative prediction of dopant enhanced solubility for a defect requires the temperature dependence of i.) any defect level in the gap and ii.) relevant parameters for reactions of the defect with other species in the host matrix. For the case of Fe in p-type Si, these parameters are E_T and E_B.

For the dopant enhanced solubility calculations contained in this paper, we focus on temperatures above 700 C where pairing has negligible impact on the solubility enhancement. Nevertheless, to generate a complete understanding of the dopant enhanced solubility at all temperatures, the exact temperature dependence of E_B should be determined.

Motion of E_T within the gap will affect the ionization statistics and thereby the dopant enhanced solubility of Fe in p-type Si. The defect level of a species which is very foreign to its host matrix is expected to behave independently from the band edges.

In Figure 5 we show calculations based on three cases of E_T behavior as temperature is increased and E_G narrows: i.) E_T stays at a constant fraction of E_G, ii.) E_T a fixed energy from the valence band edge, and iii.) E_T a fixed energy from the conduction band edge. Defect level position does affect the results, as expected, however, only the case with E_T a constant fraction of E_G is within error of the experimental data.

V. CONCLUSION

The commonly used $T^{3/2}$ model is not accurate even in the device operation regime and the available relations of Green do not extend past 500 K. We have constructed a DOS model using *ab initio* calculations and temperature appropriate Fermi-Dirac statistics to generate a more physically motivated extrapolation of DOS into the processing temperature regime. Nevertheless, much remains to be explored about high temperature effects on the band structure. The available data of dopant enhanced solubility of Fe in Si can be modeled within error assuming E_T remains at a constant fraction of E_G by either the $T^{3/2}$ model for N_C and N_V or the *ab initio* DOS. There is no evidence at this time for instability of E_T, however more accurate data for the Si DOS and E_G in the processing temperature regime will shed light on the temperature dependence of E_T.

VI. ACKNOWLEDGEMENTS

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